Abstract No. alex763

Gamma-Alumina-Supported Pt Catalysts with Extremely High Dispersions Resulting from Pt-W Interactions

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Beamline(s): X11A

γ-Al_2O_3-supported catalysts were prepared from bimetallic precursors, $\{Pt[W(CO)_3(C_5H_5)]_2(PhCN)_2\}$ and $\{Pt_2W_2(CO)_6(C_5H_5)_2(PPh_3)_2\}$, as well as from a mixture of $[PtCl_2(PhCN)_2]$ + $[W(CO)_6]$, and characterized by extended X-ray absorption fine structure (EXAFS) spectroscopy and chemisorption of H_2, CO, and O_2; the samples were reduced with H_2 at 400°C for 2 h prior to most characterizations. EXAFS data show that tungsten in either of the bimetallic precursors helped to maintain the platinum in a highly dispersed form during treatment in H_2, leading to supported platinum clusters of only about 4 to 6 atoms each, on average. EXAFS spectra measured at the Pt L_{II} edge indicate substantial Pt-W contributions in samples prepared from the bimetallic precursors, but not in samples prepared from the two monometallic precursors; the Pt-W coordination numbers in the former samples were about 2 and 1, respectively, at an average Pt-W distance of 2.71 Å. W L_{III} edge EXAFS data indicate substantial W-Pt interactions in the samples prepared from the bimetallic precursors, with an average W-Pt coordination number of about 1.0 at a distance of 2.71 Å. The results are consistent with the inference that W-Pt-W (or Pt-$(W)_2$-Pt) units in the precursor were largely retained following removal of the ligands by H_2 treatment. EXAFS data also show that the Pt-W interactions in samples prepared from the bimetallic precursors were strong enough to be largely maintained even under oxidation/reduction conditions at temperatures as high as 400°C. In addition to the metal-metal contributions, the EXAFS data show substantial interactions of both tungsten and platinum with oxygen atoms of the γ-Al_2O_3 support. The platinum clusters are inferred to be stabilized in a highly dispersed state by their interactions with tungsten cations (identified by oxygen uptake data), which are held in place by interactions with surface oxygen atoms of γ-Al_2O_3 (indicated by EXAFS data). In contrast, the sample prepared from the two monometallic precursors is characterized by a lack of Pt-W interactions (as indicated by the EXAFS spectra) and by relatively large platinum particles. The supported platinum clusters made from bimetallic precursors are characterized by lower chemisorption of CO or of hydrogen and by low catalytic activities for toluene hydrogenation at 1 atm and 60°C, relative to the values characterizing the samples made from the monometallic precursors, which incorporated larger platinum particles. On the other hand, the catalysts containing tungsten were an order of magnitude more active than Pt/γ-Al_2O_3 for hydrogenation of crotonaldehyde to give crotyl alcohol, although these catalysts were still nonselective for this reaction. The data indicate that tungsten formed isolated microscopic islands on γ-Al_2O_3, influencing the adsorption and catalysis by platinum by its proximity to the latter. Literature data indicate that other combinations of oxophilic and noble metals on oxide supports behave similarly.